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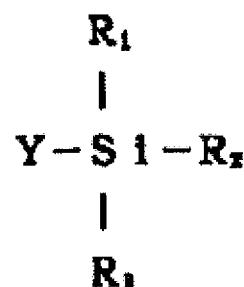
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(54) RESIN COMPOSITION

(57)Abstract:

PURPOSE: To obtain a resin composition having excellent crack resistance in soldering and moisture resistance by blending mainly a modified reactional product obtained by reacting a specified polymaleimide with a silane coupling agent.

CONSTITUTION: This resin composition is manufactured by modifying (A) a polymaleimide containing ≥ 2 maleimide groups in one molecule (e.g. N,N'- ethylenebismaleimide) by reacting 100 pts.wt. of (A) with 0.1-25 pts.wt. of (B) a silane coupling agent of the formula (Y is univalent organic acid containing amino group; R1 to R3 are H, phenyl, OR (R is H or 1-5C alkyl), etc.; at least one of R1 to R3 is OR) (e.g. 3-aminopropyltrimethoxysilane) and blending the modified product with an epoxy resin containing ≥ 2 epoxy groups in one molecule and a hardener. Optionally the component A is mixed with a phenol resin, in advance.



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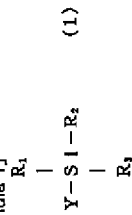
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CLAIMS

[Claim(s)]

[Claim 1] A polymaleimide compound and a general formula (1) which have two or more maleimide groups in one molecule [—izing 1]

[Chemical formula 1]



[An organic group of monovalence in which Y contains an amino group among a formula, R₁, R₂, and R₃. A hydrogen atom, a phenyl group, an alkyl group of the carbon numbers 1-6. Or a thermosetting resin composition which contains as a subject a reaction-of-degeneration thing to which are OR group (R shows an alkyl group of a hydrogen atom or the carbon numbers 1-5), and at least one of R₁, R₂, and the R₃ comes to carry out the reaction of degeneration of the silane coupling agent expressed with] which is -OR group.

[Claim 2] The thermosetting resin composition according to claim 1 which made a polymaleimide compound contain phenol resin beforehand.

[Claim 3] A resin composite by which an epoxy resin which has at least two epoxy groups being included in the thermosetting resin composition according to claim 1 or 2 and one molecule.

[Claim 4] A resin composite for semiconductor closure which contains the resin composite according to claim 1, 2, or 3 as a subject.

[Claim 5] A resin composite for semiconductor closure which contains a resin composite according to claim 1, 2, or 3 and an inorganic bulking agent as a subject.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention is concerned with the resin composite excellent in heat resistance and moisture resistance. In particular, it is related with a resin composite suitable for closing the semiconductor device of which solder heat resistance is required like a surface mount type semiconductor device.

[0002]

[Description of the Prior Art] In recent years, the heat-resistant, crack resistant, and damp-proof outstanding resin composite is called for in the field of an electric electronic component, a semiconductor, etc. For example, in the field of a semiconductor, it is in the tendency for the packaging density to the wiring board which attaches parts with the miniaturization of an electric electronic component, apparatus, and equipment and slimming down which use this to become high, and the parts itself are especially in the tendency of multi-functionalization. The material which closes this is strongly expected development of the resin composite excellent in heat resistance to the high temperature solder in the soldering process to a wiring board. As the resin composite to such a use, and what is called a resin composite for semiconductor closure, conventionally, The epoxy resin represented by *o*-cresol novolak type epoxy resin and the resin composite which uses phenol novolak resin and silica as the main ingredients as that hardening agent are excellent in respect of a moldability and reliability, and serves as the mainstream in this field. "Kakiuchi *****; the epoxy resin P80, Shokodo Co., Ltd."

[0003]

[Problem to be solved by the invention] However, speaking of a plastic molded type semiconductor device, it is changing to a surface mount type semiconductor device by the flow of the above-mentioned high-density-assembly-izing. Unlike the conventional inserting type semiconductor device, in such a surface mount type semiconductor device, the whole semiconductor device is put to the soldering temperature of not less than 200 °C by the soldering process to a substrate. By the way, the resin composite which consists of epoxy resins, if the fall of the intensity at soldering temperature is intense, and it solders while it has been in the state in which the resin closed especially absorbed moisture since the glass transition temperature is lower than soldering temperature. Resisting the stress by rapid expansion of hygroscopic water cannot be finished, a crack occurs in sealing resin, and the reliability of a semiconductor device is reduced substantially.

"magazine; the Nikkei electronics June 13, 1988 item 114 - 118-page"

Therefore, a passage given in JP H1-213335A, JP H2-254735A, and JP H2-32117A. This invention persons made glass transition temperature of sealing resin high, are the purposes of giving sufficient resin strength which overcomes the stress generated by expansion of moisture, and came in piles the research which applies imide system resin to the resin composite for closure. As a result, although intensity at the time of an elevated temperature could be made high by application of imide resin and the crack resistance at the time of soldering improved, imide system resin was inferior to the adhesive property with a semiconductor device, exfoliation occurred in the interface of an element surface and resin by the thermal shock at the time of soldering, and there was a problem that subsequent moisture resistance fell. The purpose of this invention is to provide the resin composite applicable to the surface mount type semiconductor device with which a reflow and flow soldering are made for closure by improving the solder-proof crack nature at the time of mounting, and the moisture resistance after mounting.

[0004]

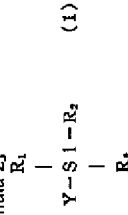
[Means for solving problem] In order to solve an aforementioned problem, as a result of repeating research

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wholeheartedly, by denaturing a polymaleimide compound by the silane coupling agent which has an amino group, this invention persons find out that the adhesive property of the semiconductor device surface and resin improves, and came to complete this invention. That is, this inventions are (1) polymaleimide compound and a general formula (1). [-izing 2]

[0005]

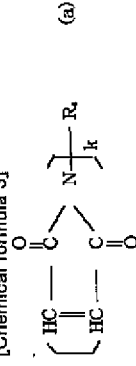
[Chemical formula 2]



the organic group of the monovalence in which Y contains an amino group among a formula, R₁, R₂, and R₃ — a hydrogen atom, a phenyl group, and the alkyl group of the carbon numbers 1-6. Or it is OR group (R shows the alkyl group of a hydrogen atom or the carbon numbers 1-5.), at least one [and] of R₁, R₂, and the R₃ -OR group — it is — the resin composite consisting of the thermosetting resin and the inorganic bulking agent which make a subject the reaction-of-degeneration thing to which it comes to carry out the reaction of degeneration of the silane coupling agent expressed. (2) The thermosetting resin composition of the above-mentioned (1) description which made the polymaleimide compound contain phenol resin beforehand, (3) A resin composite by which the epoxy resin which has at least two epoxy groups being included in a thermosetting resin composition the above (1) or given in (2), and one molecule, (4) It is a resin composite for semiconductor closure which contains the resin composite and inorganic bulking agent of a description as a subject in the resin composite for semiconductor closure which contains the resin composite of a description as a subject in the above (1), (2), or (3) and (5) above (1), (2), or (3). As a polymaleimide compound used by this invention, it is a general formula (a). [-izing 3]

[0006]

[Chemical formula 3]

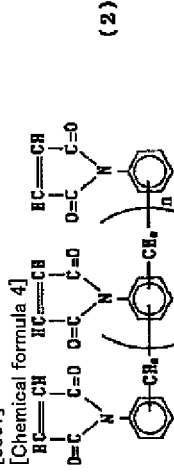


It is a polymaleimide compound expressed with (R_k) is an organic group of k value which has at least two carbon atoms, and k shows two or more positive integers among a formula), and it is altogether usable if it is a compound which has two or more maleimide groups in one molecule. As such a polymaleimide compound, it is N,N', for example, - Ethylenbis maleimide, N,N'- Hexamethylene bismaleimide, N,N' - (1,3-phenylene) Bismaleimide, N,N'-[1,3-] (2-methylphenylene) bismaleimide, N,N'-(1,4-phenylene) bismaleimide, screw (4-maleimide phenyl) Methane, Screw (3-methyl-4- maleimide phenyl) Methane, screw (4-maleimide phenyl) Ether, Screw (4-maleimide phenyl) A sulfone, screw (4-maleimide phenyl) Sulfide, Screw (4-maleimide phenyl) ketone, screw (4-maleimide cyclohexyl) Methane, 1,4-screw (maleimide methyl) Benzene, 1,3-screw (maleimide methyl) Cyclohexane, 1,4-screw (maleimide methyl) Cyclohexane, 1,4-screw (maleimide methyl) Benzene, bis[4 - (3-maleimide phenyl) methylene] methane, bis[4 - (4-maleimide phenyl) phenyl] methane, 1,1-bis[4 - (3-maleimide phenyl) ethane, 1,1-bis[4 - (4-maleimide phenyl) phenyl] ethane, 1,2-bis[4 - (3-maleimide phenyl) ethane, 1,2-bis[4 - (4-maleimide phenyl) phenyl] ethane, 2,2-bis[4 - (3-maleimide phenyl) propane, 2,2-bis[4 - (4-maleimide phenyl) phenyl] propane, 2,2-bis[4 - (3-maleimide phenyl) butane, 2,2-bis[4 - (4-maleimide phenyl) phenyl] butane, 2,2-screw [4-(3-maleimide phenyl) phenyl]-1,1,1,3,3,3-hexafluoropropane, 2,2-screw [phenyl [4 - (4-maleimide phenyl)]]-1,1,3,3,3-hexafluoropropane, 4,4'-screw (3-maleimide phenyl) Biphenyl, 4,4' - Screw (4-maleimide phenyl) Biphenyl, bis[4 - (3-maleimide phenyl) phenyl] ketone, bis[4 - (4-maleimide phenyl) phenyl] ketone, A bis[4 - (3-maleimide phenyl) phenyl] sulfide, Bis[4 - (4-maleimide phenyl) phenyl] SURUIDO, A bis[4 - (3-maleimide phenyl) phenyl] sulfoxide, A bis[4 - (4-maleimide phenyl) phenyl] sulfoxide, A bis[4 - (3-maleimide phenyl) phenyl] sulfone, A bis[4 - (4-maleimide phenyl) phenyl] ether, 1,4-bis[4-(4-maleimide maleimide phenyl) phenyl] ether, Bis[4 - (4-maleimide phenyl) phenyl] ether, 1,4-bis[4-(4-maleimide

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phenoxy)-alpha and alpha - dimethylbenzyl] benzene, 1,3-bis[4-(4-maleimide phenoxy)-alpha and alpha - dimethylbenzyl] benzene, 1,4-bis[4-(3-maleimide phenoxy)-alpha and alpha - dimethylbenzyl] benzene, 1,3-bis[4-(3-maleimide phenoxy)-alpha and alpha - dimethylbenzyl] benzene, 1,4-bis[4-(4-maleimide phenoxy)-3,5-dimethyl- alpha and alpha - dimethylbenzyl] benzene, 1,3-bis[4-(4-maleimide phenoxy)-3,5-dimethyl- alpha and alpha - dimethylbenzyl] benzene, 1,4-bis[4-(3-maleimide phenoxy)-3,5-dimethyl- alpha and alpha - dimethylbenzyl] benzene, 1,3-bis[4-(3-maleimide phenoxy)-3,5-dimethyl- alpha and alpha - dimethylbenzyl] benzene, a general formula (2) [-izing 4]

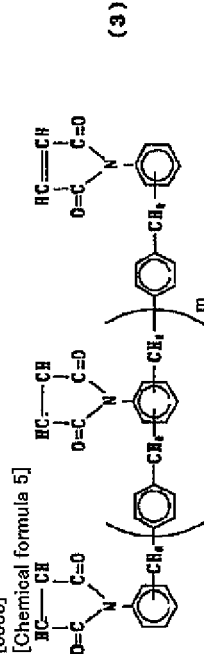
[0007]



(2)

The polymaleimide compound expressed with (the inside of a formula and n are 0-10 by average value), and a general formula (3) [-izing 5]

00081



(3)

The polymaleimide compound etc. which are expressed with (the inside of a formula and m are 0-10 by average value) are mentioned. These polymaleimide compounds may be used independently, or two or more kinds may be mixed and they may be used. The silane coupling agent used for this invention is expressed with the above-mentioned general formula (1).

the above mentioned general formula (I) are: 3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-aminopropyl dimethoxymethylsilane, 3-aminopropyl diethoxymethylsilane, 3-aminopropyl dimethoxysilane, 3-(2-aminoethyl aminomethyl) trimethoxysilane, 3-(2-aminoethyl aminopropyl) trimethoxysilane, 3-(2-aminoethyl aminomethyl) dimethoxymethylsilane, 3-[2-(2-aminoethyl amino) propyl] trimethoxysilane, 3-phenylamino propyltrimethoxysilane, 3-benzylamino propyltrimethoxysilane, 3-cyclohexylamino propyltrimethoxysilane, N-(3-triethoxy silyl propyl) urea, N-(3-triethoxy silyl propyl)-p-nitrobenzamide, 2-(2-aminoethyl thioethyl) triethoxysilane, 2-(2-aminoethyl thioethyl) diethoxymethylsilane, 3-piperazino propyltrimethoxysilane, a dimethoxymethyl 3-piperazino propylsilane, 3-dibutylamino propyltrimethoxysilane etc. are raised, and these things are independent or are used by two or more sorts. The reaction of degeneration of a polymaleimide compound and a silane coupling agent carries out heating mixing of a polymaleimide compound, a silane coupling agent, the polymaleimide compound, phenol resin and a silane coupling agent, although it is the range of 0.1-25 mixture ratio of a polymaleimide compound and a silane coupling agent, to a mixture ratio of 0.1-25 copies of silane coupling agents and restriction in particular does not have the mixing ratio of phenol resin to a polymaleimide compound to 100 copies (a weight section and the following — the same) of polymaleimide compounds, those total quantities are preferred and about 1 to 50 weight % is practical. The loadings of a silane coupling agent are 0.1. A reaction of degeneration is insufficient for the case of less than a part, and if it exceeds 25 copies, a silane coupling agent independent reaction will start and it will have an adverse effect on moisture resistance.

have an adverse effect on modulus of elasticity.

cresol, resorcinol, and naphthol. Acetaldehyde, benzaldehyde, hydroxybenzaldehyde. The novolak type epoxy resin derived from novolak resin which is a resultant of aldehyde, such as guru oxal and alkanedial. And the aralkyl type epoxy resin derived from aralkyl resin which is a resultant of the above-mentioned phenols and an aralkyl alcohol derivative is preferred from a point of heat resistance and an electrical property.

[0011] In addition, the epoxy resin derived from the compound which has two or more active hydrogen groups in one molecule. For example, bisphenol A, the bisphenol F, resorcinol, screw hydroxydiphenyl ether, 4,4'-screw hydroxy-3,3',5,5'-Tetramethyl biphenyl, Tetra bromine bisphenol A, dihydroxynaphthalene, a trihydroxy phenylmethane, Polyhydric phenol, such as tetra hydroxyphenyl ethane and alkane tetrakis phenol; Ethylene glycol, Neopentyl glycol, glycerol, trimethylolpropane, pentaerythritol, Polyhydric alcohol classes, such as a diethylene glycol and a polypropylene glycol; Ethylenediamine, Amines, such as aniline and bis(4-aminophenyl)methane; Adipic acid. The epoxy resin etc, which are produced by making polyvalent carboxylic acid, such as phthalic acid and isophthalic acid, epichlorohydrin, or 2-methyl epichlorohydrin react are mentioned. One kind of these epoxy resins or two kinds or more are used.

[0012] It can also be used for the aforementioned epoxy resin with silicone compounds, such as the shape of oil, and the shape of rubber, denaturalizing. For example, Provisional Publication No. 270617 [62 to I, Provisional Publication No. 273222 [62 to], it is silicone modified epoxy resin

manufactured by distributing the particles of silicone polymer in the reactant of an epoxy resin and vinyl polymer. Although publicly known things, such as phenols, amines, and an acid anhydride, can be used as a hardening agent of said epoxy resin, phenol resin is used most preferably. For example, phenols and formaldehyde, such as phenol, cresol, resorcinol, and naphthol, Acetaldehyde, benzaldehyde, hydroxybenzaldehyde, Novolak resin which is a resultant of aldehyde, such as gura oxal and alkanedial, And the polyhydric phenol which are the resultants of the above-mentioned phenols and an alkaly alcohol derivative, such as aralkyl resin, a trihydroxy phenylmethane, tetra hydroxyphenyl ethane, and tetrakis phenol, is mentioned, and these one kind or two kinds or more are used. When using an epoxy resin together in the reaction-of-degeneration thing to which it comes to carry out the reaction of degeneration of the silane coupling agent expressed with a polymaleimide compound and the above-mentioned general formula (1) in the constituent of this invention, it is the reaction-of-degeneration thing 100. As opposed to a weight section, the total quantity of an epoxy resin and a hardening agent --- 10-500 weight section --- it is 25-300 weight section preferably, moreover --- the rate of an epoxy resin and a hardening agent receives the epoxy group of an epoxy resin --- a hardening agent --- equivalent ratio --- the range of 0.1-10 --- it is the range of 0.5-2.0, preferably.

[0013] The inorganic bulking agent used in the constituent of this invention, Although the thing of an inorganic granular material or a fibrous body is usable, for example, there are fibrous bodies, such as granular material; glass fibers, such as crystalline silica, fused silica, alumina, silicon nitride, silicon carbide, talc, silicic acid calcium, calcium carbonate, mica, clay, and a titanium white, and carbon fiber. The silica powder of the crystallinity from a point of a coefficient of thermal expansion and thermal conductivity and melting nature is preferred. The mixture of the silica powder of the fluid point at the time of shaping to a globular form or a globular form, and an infinite form is preferred. To the thermosetting resin 100 weight section which makes a reaction-of-degeneration thing a subject, it is required to be 100-900 weight section, and the loadings of an inorganic bulking agent are 200-600 preferably. It is a weight section. The above-mentioned inorganic bulking agent may reform the surface beforehand by finishing agents, such as the Silang system, a titanate system, an aluminate system, and a zirconaluminate system coupling agent, apart from the silane coupling agent used for this invention as occasion demands. The Silang system coupling agent is preferred also in it, and the Silang system coupling agent which has a reactant functional group, especially is the most preferred.

Group, especially in the most preferred one. [0014]As an example of this Slang system coupling agent, Vinyltrimethoxysilane, vinyltriethoxysilane, N-(2-aminoethyl)3-aminopropyl methyl dimethoxysilane, N-(2-aminoethyl)3-aminopropyl trimethoxysilane, 3-aminopropyl triethoxysilane, 3-anilino propyltrimethoxysilane, 3-glycidyxypropyltrimethoxysilane, 3-glycidoxypropylmethyl dimethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, 3-methacryloxy propyl trimethoxysilane, 3-mercaptopropyltrimethoxysilane, etc. can be mentioned, and these one kind or two kinds or more are used.

[0115] In hardening a resin composite, in this invention, It is desirable to make a hardening accelerator contain and as this hardening accelerator, Imidazole derivatives, such as 2-methylimidazole, 2-methyl-4-ethylimidazole, and 2-heptadecylimidazole; Triethanolamine, Amines, such as a triethylene diamine and N-methyl morpholine; Tributyl phosphine, Organic phosphine, such as triphenyl phosphine and tritriyl phosphine; Tetraphenyl phosphonium tetraphenylborate, Tetraphenylboron salts, such as triethyl ammonium

tetraphenyl borate; the 1,8-diaza-bicyclo (5, 4, 0) undecene 7 and its derivative are mentioned. These hardening accelerators may be used independently, may use two or more kinds together, and can also use organic peroxide and an azo compound together if needed. The content of these hardening accelerators is used in the range of 0.01 to 10 weight section to thermosetting resin 100 weight section which makes a reaction-of-degeneration thing a subject.

[0016]The resin composite of this invention if needed besides the various above-mentioned ingredients Diallyl phthalate, Reactive diluent; several-kinds silicone oil generally used to inide resin, such as triallyl isocyanurate and o,o'- diarylbisphenol A; Fatty acid, Fire retardant, such as mold lubricant, bromine compounds, such as fatty acid salt and a wax, antimony, and a phosphorus; colorant, such as carbon black, etc. can be blended, and it can mix and mull, and can be considered as a molding material.

[0017]

[Working example]Hereafter, an embodiment explains this invention concretely. In an embodiment, the test method of the performance of a constituent is as follows.

- glass-transition-temperature: --- TMA method and bending strength: --- JIS K-6911 and solder immersion test: --- immediately after neglecting 25 semiconductor devices for an examination to 85 ** and 85% of constant temperature/humidity chamber for 168 hours, it is immersed in a 260 ** molten solder bath for 10 seconds.

Then, the number of the semiconductor devices which the crack generated in package resin was counted. The damp-proof test after solder immersion : In a solder immersion test, a crack the semiconductor device for an examination by which it was not generated - 121 **, It is neglected in a 2-atmosphere pressure cooker tester, electrical continuity is checked for every fixed time, and the poor incidence rate by the corrosion of aluminum wiring measures time to reach to 50%.

[0018]Example A-G of manufacture (manufacture of reaction-of-degeneration thing A-G)

The polymaleimide compound was inserted in the reaction vessel equipped with an agitator, a thermometer, and a condenser, it warmed at 160 **, the silane coupling agent was inserted so that it might become the presentation of A-G of the 1st table, and you made it react for 3 minutes, it cooled immediately, and reaction-of-degeneration thing A-G was obtained.

[0019]Example H-K of manufacture (manufacture of reaction-of-degeneration thing H-K)

A polymaleimide compound and phenol resin are inserted in the reaction vessel equipped with an agitator, a thermometer, and a condenser, and it warms at 160 **, and is the 1st table. The silane coupling agent was inserted so that it might become the presentation of H-K of [Table 1], and you made it react for 5 minutes, it cooled immediately, and reaction-of-degeneration thing A-G was obtained.

[0020]

[Table 1]

第1表

変性反応物	ポリマレイミド化合物 (重量部)	シランカップリング剤 (重量部)	ノボラック型フェノール樹脂 (重量部)
A	ポリマレイミド化合物(1) 100	KBM6035	
B	ポリマレイミド化合物(1) 100	KBM6025	
C	ポリマレイミド化合物(1) 100	SZ-60835	
D	ポリマレイミド化合物(1) 100	A-1875	
E	ポリマレイミド化合物(2) 100	KBM6035	
F	ポリマレイミド化合物(2) 100	SZ-60835	
G	ポリマレイミド化合物(2) 100	A-1875	
H	ポリマレイミド化合物(1) 100	KBM6035	20.7
I	ポリマレイミド化合物(1) 100	SZ-60835	20.7
J	ポリマレイミド化合物(2) 100	KBM6035	20.7
K	ポリマレイミド化合物(2) 100	SZ-60835	20.7

[0021]Embodiments 1-9 and the comparative example 1 ~ the 8 2nd table. The compound of the presentation (weight section) shown in [Table 2] was mixed with the Henschel mixer, and melting and the mull of were done for 3 minutes with a further 100-130 ** hot calender roll. This mixture was cooled and ground, was tableted and the molding resin composition was obtained. The following were used for the raw material used all over the 1st and 2nd table.

- Polymaleimide compound (1); bis(4-maleimide phenyl)methane (product made from Mitsui Toatsu Chemicals Chemistry)
- Polymaleimide compound (2); 4,4'-bis(3-maleimide phenoxy)BIFU ENIRU (made by Mitsui Toatsu Chemicals, Inc.)
- Epoxy resin; o-cresol novolak type epoxy resin (ECON-1020, Nippon Kayaku Co., Ltd. make)
- Bromine-ized epoxy resin; bromine-ized phenol novolak type epoxy resin (BREN-S, Nippon Kayaku Co., Ltd. make)
- Hardening agent; novolac type phenol resin (PN-80, Nippon Kayaku Co., Ltd. make)
- Inorganic bulking agent (1); globular form fused silica with a mean particle diameter of 20 micro (Hari Mick S-CO, Micron Make)
- Inorganic bulking agent (2); infinite form fused silica with a mean particle diameter of 13 micro (made in fuse REXX RD-8 Tatsumori)
- Silane coupling agent; 3-(2-aminoethyl aminopropyl) trimethoxysilane (KBM603, Shin-Etsu Chemical Co., Ltd. make)
- Silane coupling agent; 3-(2-aminoethyl aminopropyl) methyl dimethoxysilane (KBM602, Shin-Etsu Chemical Co., Ltd. make)

